Anomalous θ swelling of macromolecules: new method of calculation

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A new method is presented for the calculation of the anomalous θ swelling of macromolecules with high average monomer concentration in the unperturbed polymeric coil. This method is applied to determine the θ swelling of two-dimensional coils and of star-branched macromolecules. The results for the swelling coefficient at the θ temperature (α_θ) are: $\alpha \sim N^{1/4}$ for two-dimensional coils and $\alpha_\theta^8 - \alpha_\theta^6 \sim f^4$ for star-branched macromolecules, where N is the total number of monomers in the macromolecule and f is the number of branches.

INTRODUCTION

It is generally assumed that at the θ temperature the conformation of a linear macromolecule is unperturbed by excluded volume effects[1]. The reason for this is the low value of the average monomer concentration in the polymeric coil: at the θ temperature the effect of binary interactions between monomers vanishes and, due to the low concentration, the effect of higher order interactions is always negligible[2].

However, if the average monomer concentration in the unperturbed polymeric coil is higher than for the usual linear macromolecule, the conformation at the θ temperature is no longer ideal, higher-order interactions become important and the coil shows anomalous θ swelling with respect to the unperturbed dimensions. Here, we shall consider two situations of this kind: anomalous θ swelling of two-dimensional coils (the two-dimensional cause can be realized, for example, if the macromolecule is strongly adsorbed on a flat surface); and anomalous θ-swelling of star-branched macromolecules which has frequently been observed in experiments[2] and has formed the subject of theoretical discussion[3-5].

The aim of this paper is to present a new general method of calculating the anomalous θ swelling and to apply this method to the two cases cited.

It is necessary to choose the specific polymer chain model (this can be done without any loss of generality[6] and we shall use the standard Gaussian model[6], in which the chain is represented as a sequence of 'beads' (monomers) strung on a flexible (Gaussian) immaterial filament. We shall use the following notation: N is the total number of monomers in the macromolecule; f is the number of branches (for the star-branched macromolecules); a is the mean square distance between two subsequent along the chain monomers; B and C are the second and the third virial coefficients of the interaction of monomers (accounting only for binary and ternary interactions will be sufficient for our purposes). We shall consider only flexible-chain macromolecules, where the following estimations are valid[6] near the θ-temperature:

$$B \sim a^d \tau; \quad C \sim a^{2d} \tag{1}$$

here $\tau = (T-\theta)/\theta$; T is temperature; and d is the spatial dimensionality (equations (1) are written for arbitrary d, because we shall consider the two-dimensional case, $d = 2$).

GENERAL OUTLINE OF THE METHOD

At the θ temperature the macromolecule is always in the coiled state. However, it should be recalled that slightly below the θ point macromolecules becomes globular, the coil–globule transition for the flexible linear macromolecule in three-dimensional space being a second order phase transition of width $\Delta T \sim \theta \cdot N^{-1/2}$[2]. At the upper boundary of the temperature interval ΔT (at the θ temperature) the macromolecule is coiled and at the lower boundary (at $|\tau| \sim N^{-1/2}$) it is globular. In the interval ΔT the macromolecular conformational characteristics undergo a smooth crossover from coil values to globular ones, and thus the globular characteristics at $|\tau| \sim N^{-1/2}$ are of the same order of magnitude as the coil characteristics at the θ temperature[2]. Consequently, we can, in principle, estimate the macromolecular dimensions at the θ temperature if the globular radius at $|\tau| \sim N^{-1/2}$ is known.

For linear flexible macromolecules in three-dimensional space this estimation is not helpful because the corresponding result $R \sim aN^{1/2}$(R represents macromolecular dimensions) can be obtained much more simply. However, for the cases under considerations the analogous procedure leads to non-trivial results, since the construction of the theory of globules for these cases requires only some non-essential generalizations of the theory of ref 2 and, at the same time, the theory of the θ behaviour of the coils is much more complex.

The method applied in order to determine the anomalous θ swelling is as follows. First, it is necessary to develop the theory of globules and of the coil globule transition for the case under consideration. If it turns out that the coil–globule phase transition is second order and that it takes place in the temperature interval, ΔT, with upper boundary the θ point, then for the estimation of the θ dimensions of the coil it is enough to estimate the globule radius at the lower boundary of the interval ΔT.

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θ SWELLING OF THE TWO DIMENSIONAL COILS

We consider the problem of a linear polymer chain in two-dimensional space. The anomalous θ swelling in this case is due to the fact that the average monomer concentration n in the unperturbed coil is not small ($n \sim N/R^2 \sim N/Na^2 \sim 1/a^2$) and so higher-order interactions are important.

As for the case $d=3$, it is first necessary to determine the free energy of interaction between monomers in the globule using the volume approximation (F_{int}) and the surface free energy of the globule (F_s). It is easy to see that the expression for the free energy F_{int} does not depend on d and remains the same as in the three-dimensional case, i.e.[2] at $|\tau| \ll 1$:

$$F_{int} = -NT\frac{B^2}{4C} \sim -NT\tau^2 \tag{2}$$

where we have used the estimations of equations (1). At the same time, the surface free energy F_s for $d=2$ can be written in the form $F_s \sim R\sigma$, where σ is the surface tension coefficient. It is clear that the value of σ does not depend on d and is determined by the equation (5.7) of ref 2:

$$\sigma = \frac{aB^2T}{8C^{3/2}} \sim \frac{T}{a}\tau^2 \tag{3}$$

The globular radius R can be found from the equality $n \sim N/R^2$. According to the equation (5.3) of ref 2 $n \sim -B/2C \sim |\tau|/a^2$. Thus we have:

$$R \sim \left(\frac{Na^2}{|\tau|}\right)^{1/2} \tag{4}$$

and, finally:

$$F_s \sim R\sigma \sim \left(\frac{Na^2}{|\tau|}\right)^{1/2}\frac{T}{a}\tau^2 \tag{5}$$

The total free energy of a globular macromolecule is the sum of F_{int} and F_s: $F = F_{int} + F_s$.

The temperature at the coil-globule transition, τ_c ($\tau_c = (T_c - \theta)/\theta$) can be determined from the condition $F=0$[2]. Using the equations (2) and (5) we have:

$$|\tau_c| \sim 1/N; \quad \tau_c < 0 \tag{6}$$

Using equation (6) the expression for the globular free energy can be written in a form analogous to equation (5.8) of ref 2:

$$F \sim -NT\tau^2\left(1 - \left|\frac{\tau_c}{\tau}\right|^{1/2}\right) \tag{7}$$

The width of the coil–globule transition ΔT can be determined from the condition[2]:

$$|F(T_c - \Delta T)| \sim T \tag{8}$$

From equation (7) it is easy to obtain in the asymptotic limit $N \gg 1$:

$$\Delta T/\theta \sim 1/N^{1/2} > |\tau_c| \tag{9}$$

From equation (9) it can be seen that (i) since $\Delta T \to 0$ as $N \to \infty$, according to the terminology introduced in ref 2 the coil–globule transition is in this case the phase transition; (ii) since $\Delta T/\theta \gg |\tau_c|$, when the θ temperature is approached from below, the globular structure is 'destroyed' due to fluctuations before the point where surface terms become essential; thus the surface free energy can be neglected over the region in which the globule exists and the coil–globule phase transition is second order (compare with ref 2).

Thus, for a linear two-dimensional polymer chain the coil–globule phase transition is second order, and takes place in the temperature interval $\Delta T \sim \theta N^{-1/2}$, with an upper boundary of the θ point. Thus, we can use the method described above. From equation (4) we obtain for the radius of the two-dimensional globule at $|\tau| \sim \Delta T/\theta \sim N^{-1/2}$:

$$R \sim N^{3/4}a \tag{10}$$

According to the section above we can conclude that equation (10) also gives an estimation for the θ dimensions of the polymeric coil at $d=2$. The corresponding coefficient of anomalous θ swelling is:

$$\alpha_\theta \equiv R/R_0 \sim N^{1/4} \tag{11}$$

where $R_0 \sim N^{1/2}a$ denotes the unperturbed dimensions of the coil. We see that in the two-dimensional case there is no temperature at which the chain would be ideal: even at the θ temperature the coil shows some swelling.

Further, we note that the result (10) for the anomalous θ swelling is exact in the sense that the exponent ν obeys the dependence $R \sim N^\nu$. From this, we can deduce the following two conclusions concerning the value of ν for the two-dimensional excluded volume problem (i.e. for the two-dimensional chain in a good solvent).

(i) Since the swelling in the good solvent must be more pronounced than at the θ point, we obtain $\nu \geq 3/4$ as the *exact* inequality for the two-dimensional excluded volume exponent.

(ii) $R \sim N^{3/4}$ was observed in the majority of computer simulations of the two-dimensional excluded volume problem[7], and thus it is natural to assume that for the two-dimensional coil ν is exactly equal to 3/4 in the good solvent as well as at the θ point. (However, this assumption is strictly proven only for the θ temperature.)

θ SWELLING OF THE STAR-BRANCHED MACROMOLECULES

We now return to three-dimensional space and consider the anomalous θ swelling of star-branched macromolecules, which occurs because the average monomer concentration within the branched macromolecule is higher than within the linear species.

There are two theories in the literature concerning the anomalous θ behaviour of branched macromolecules. One[3] is based on the smoothed density model, and the other[5] is based on the concept of quasimonomers. In application to star-branched macromolecules with f branches both theories give the same result for the coefficient of the anomalous θ swelling:

$$\alpha_\theta^8 - \alpha_\theta^6 \sim f^3; \quad \alpha_\theta \equiv R/R_0 \tag{12}$$

where R and R_0 are the actual macromolecular dimensions and the unperturbed ones respectively. With the help of the method proposed above we shall show that the equation (12) is not exact (see equation (15) below). The theory in ref 5 does not give the correct answer, because parallel with the concept of quasimonomers it uses Flory's arguments, which may not be valid[8].

In order to apply the method described above it is first necessary to develop the theory of the coil–globule transition for star-branched macromolecules. It is important to emphasize that since the correlation radius in the globule, ξ, is always much less than R (ref 2), the globular structure, which is determined by properties of order $\sim \xi$, is insensitive to the topology of the connectivity of monomers in star-branched macromolecules, which becomes apparent only on the scale $\sim R$. Thus, as soon as the star-branched macromolecule is in the globular state, it is described by the same formulae as the linear macromolecule with the same N. In particular, for a star composed of flexible chains, the coil–globule phase transition is second order, with width $\Delta T \sim \theta N^{-1/2}$ where the θ temperature is the upper boundary of the interval ΔT [2]. Since the average monomer concentration in the globule is $n \sim |\tau|/a^3$ [2], we obtain for the globular radius at the lower boundary of the interval ΔT(i.e. at $|\tau| \sim N^{-1/2}$):

$$R \sim \left(\frac{N}{n}\right)^{1/3} \sim \left(\frac{Na^3}{|\tau|}\right)^{1/3} \sim N^{1/2}a \tag{13}$$

According to the theory above, equation (13) gives an estimation for the θ dimensions of the star-branched macromolecules. Since $R_0 \sim (N/f)^{1/2}a$, we conclude that:

$$\alpha_\theta \equiv R/R_0 \sim f^{1/2} \tag{14}$$

In the derivation of the equation (14) we have used only estimations of the orders of magnitude. Hence, equation (14) must be regarded as the asymptotic swelling law at $f \gg 1$. In order to cover the range $f \sim 1$ it is natural to suppose that $\alpha_\theta(f)$ has the standard form $\alpha_\theta^8 - \alpha_\theta^6 \sim f^6$ (compare with equation 12), where the exponent b must be chosen to give the correct asymptotic form (equation 14): $b = 4$. Thus, we finally obtain:

$$\alpha_\theta^8 - \alpha_\theta^6 \sim f^4 \tag{15}$$

Thus, the present theory predicts that the θ swelling exhibits a stronger dependence on f than predicted previously[3,5] (compare equations 12 and 15). Experimental evidence for this prediction can be obtained from the *Figure 7* of ref 3, where the value of $\alpha_\theta^8 - \alpha_\theta^6$ is plotted *versus* f^3. It can be seen that the plot tends to deviate from a straight line in the direction of a more strong dependence of $\alpha_\theta^8 - \alpha_\theta^6$ on f. However, more accurate measurements are needed to give experimental verification of the result in equation (15).

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